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Mechanisms of silicon nitride etching by electron cyclotron resonance plasmas using SF_6- and NF_3-based gas mixtures

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The results of a study of SiN_x, SiO_2, and Si etching in a high-density electron cyclotron resonance plasma using mixtures containing SF_6, NF_3, N_2, O_2, and Ar are presented. Higher selectivities of SiN_x etching over SiO_2 (up to ~100) were achieved with NF_3, while higher selectivities over Si (up to 5–10) were obtained with SF_6-based mixtures. Plasma and surface processes responsible for etching are analyzed, and mechanisms of nitride etching in NF_3-based plasmas are proposed. © *2004 American Vacuum Society.* [DOI: 10.1116/1.1701858]

I. INTRODUCTION

For many thin-film technologies, selectivity of etching is a critical parameter. In plasma etching, the selectivity is determined by the chemistry of processes occurring on surfaces and involving reactive radicals produced in the plasma which, in turn, are controlled by a proper choice of etching gases. Surface reactions and etch product removal can be accelerated by energetic plasma ions. However, the etch selectivity tends to reduce under strong ion bombardment. Reactive radicals result basically from dissociation of feed gas molecules by electron impact. However, in some cases, new reaction intermediates can be formed by gas-phase reactions between feed gases and/or their dissociation products in the plasma. Development of selective etch processes is particularly challenging for compound materials whose components require different etch chemistries.

For silicon nitride etching technology, high selectivities over both silicon oxide and silicon are usually required.[1–3] In fluorine-based etching of SiN_x, a critical step is the removal of nitrogen strongly bound to silicon atoms. Subsequently, surface Si atoms can be readily etched by F radicals. In a recently developed approach,[4–6] plasmas rich in O_2 and N_2 with only small additions of fluorine-containing gases (CF_4, NF_3, or SF_6) were employed. NO molecules formed in the gas phase reacted quickly with surface N atoms, forming N_2 molecules according to the reaction

$$N_{(surface)}+NO_{(gas)}\rightarrow O_{(surface)}+N_{2(gas)}, \quad (1)$$

which promotes enhanced removal of nitrogen from the nitride surface. This reaction is highly exothermic (the energy released is ~7.0 eV) accelerating the net nitride etching process considerably. The etching can be very selective, as in the O_2-based mixtures both silicon oxide and silicon etch very slowly.

Compared with fluorocarbon gases, NF_3 and SF_6 have advantages of shorter atmospheric lifetimes and avoidance of contamination residues. NF_3-based low-density plasmas are also widely used for cleaning purposes, to remove silicon nitride and oxynitride residues in chemical-vapor-deposited (CVD) plasma tools.[7] Mechanisms responsible for selective nitride etching in O_2/N_2-rich plasmas were analyzed in a number of studies,[4,5] with the main emphasis on the surface chemistry. On the other hand, the gas-phase mechanisms are not well understood and require further investigation. It is known that these mechanisms differ significantly in high- and low-density plasmas,[6–8] and may depend on diluent or buffer gases.[7]

The main objective of the present work is to study mechanisms responsible for selective silicon nitride etching using NF_3- and SF_6-based plasmas in an electron cyclotron resonance (ECR) high-density plasma reactor.

II. EXPERIMENT

The ECR plasma source of Plasma Therm SLR770 used here[9] consists of two parts: a plasma chamber where a dense plasma is generated, and a process chamber where the plasma flows downstream to a lower electrode used as a sample holder. An additional rf source is used to control the electrode bias and thus, the energy of ions bombarding the sample surface.

Experiments were carried out with three kinds of samples: (i) monocrystalline (100) Si, (ii) SiO_2 films (1 μm thick)

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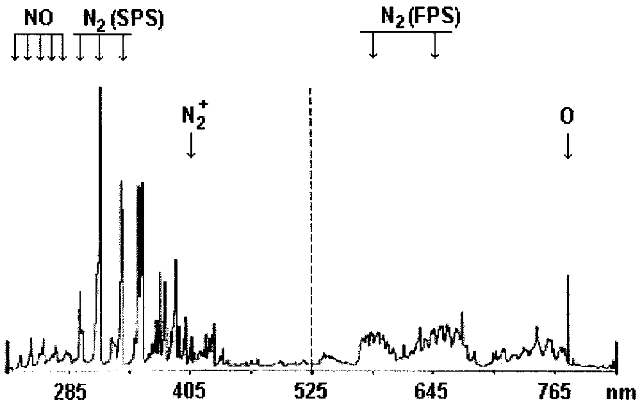

FIG. 1. Plasma emission in 225–825 spectral range. Plasma composition: $NF_3/O_2/N_2=2.5/50/50$ sccm.

produced by thermal oxidation of silicon substrates, and (iii) SiN_x films (up to 0.5 μm thick) deposited by a low-pressure CVD process over thin oxide films using silicon substrates. Mixtures of gases containing N_2, O_2, Ar, NF_3, and SF_6 in different compositions were used. In most experiments, etching time was selected to be 2 to 3 min, to avoid complete resist (AZ5214) removal during the process. A scanning spectrometer was used for diagnostic of optical emission from the plasma in a 200–900 nm spectral range.

III. RESULTS AND DISCUSSION

Spectroscopic analysis has shown that spectra emitted from the plasmas containing NF_3, O_2, and N_2 are very similar to those observed for the $SF_6/O_2/N_2$ mixtures[6] with only minor differences. An example of the spectrum emitted by $NF_3/O_2/N_2$ plasma is shown in Fig. 1. It is important to note that our actinometry measurements using Ar 750 nm line (see Ref. 6 for details of the technique) have shown that under the same plasma conditions, NF_3 is usually 30%–50% less efficient as a supplier of atomic fluorine than SF_6. We have also found that the characteristic emission of NF radicals at ~529 nm[8] is very weak and is difficult to detect due to strong masking from N_2 molecular emission. As for NO production, in both cases almost equally intense NO molecular γ-system emission below 285 nm is detected. Moreover, the NO γ system is also observed in NF_3/O_2 plasmas, along with relatively strong N_2 and N optical emission. This is consistent with observations[7,8] that NF_3 easily dissociates in plasmas, and proves that efficient NO formation occurs in reactions of oxygen with NF_3 and its dissociation products (molecular and atomic nitrogen). Similarly to the SF_6 case,[6] small additions of NF_3 to O_2/N_2 mixtures lead to a considerable (3 to 5 times) reduction of the NO emission. Since both NF_3 and SF_6 are strongly electronegative gases, that is likely due to electron attachment and corresponding reduction of the electron density. This, in turn, results in reduced production of NO in a reaction

$$N_2(v \geqslant 13)+O \rightarrow NO+N, \tag{2}$$

where only vibrationally "hot" nitrogen molecules, excited mostly in collisions with low-energy electrons, are involved.[6,10,11] Participation of metastable N_2 molecules in generation of NO may be also important, especially for plasmas with reduced electron density:

$$N_2(A\,^3\Sigma_u^+)+O \rightarrow NO+N. \tag{3}$$

Note that N_2 metastables are produced mostly in collisions with high-energy electrons, so that the mechanism (3) is less affected by the process of electron attachment (in the presence of electronegative gases), which is known to have higher cross sections for "cold" electrons. A reaction involving atomic nitrogen was shown to be of less importance for the conditions of a dc discharge, except for oxygen-rich plasmas:[10,11]

$$N+O_2 \rightarrow NO+O. \tag{4}$$

Stronger NO emission is observed in the upper part of the reactor. This indicates that NO radicals are produced mostly in the upper high-density plasma region and its regeneration in the downstream low-density plasma [most likely, in reaction (3) with N_2 metastables][6] does not compensate losses occurring mainly due to a rapid reaction[3,10]

$$NO+N \rightarrow N_2(v)+O, \tag{5}$$

and to a lesser extent, due to a three-body reaction,[3,11] which is more important for high-pressure conditions:

$$NO+O+M \rightarrow NO_2+M, \tag{6}$$

where $M=N_2$ or O_2.

While emission spectra from SF_6- and NF_3-based plasmas appear to be very similar, their etching characteristics differ essentially. Some results showing the etch-rate dependencies on the main plasma parameters are shown in Figs. 2–8. Note that under the ECR conditions, where a dc bias between the downstream plasma and the electrode is relatively low (it can be as low as ~20 eV), the etching selectivity over oxide is quite high. When no or low rf power was applied to the electrode, the oxide etching was very slow or practically stopped (etch rates are as low as 0.25–1 nm/min), so the oxide etch rate is not shown in most plots. Under these conditions, the maximum SiN_x-to-SiO_2 etch selectivities as high as ~30–50 and ~50–100 were obtained for SF_6- and NF_3-based mixtures, respectively. The maximum etching selectivities over Si were found to be lower: up to 5–10 and 1.5–2.5 for the SF_6 and NF_3 cases, respectively. With dc bias higher than 30–40 V (at rf power of 40–100 W), considerable rise of oxide etch rates to the level of 5–10 nm/min was observed.

As it was shown earlier for SF_6-based mixtures,[6] better selectivities over both SiN_x and Si were achieved at higher pressures (50–70 mTorr), near the upper pressure limit for the ECR source used. This is evidently due to reduced ion bombardment in the downstream region, as the ratio of radicals to ions arriving at the electrode rises with pressure. In particular, at higher pressures, a smaller fraction of fluorine

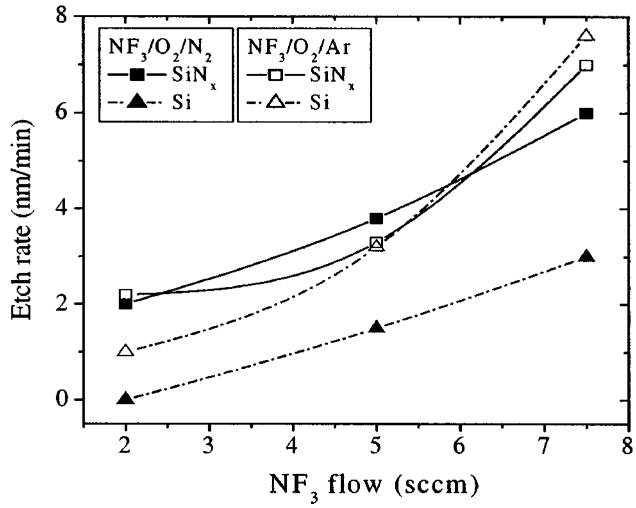

FIG. 2. Etch-rate dependencies on NF_3 flow rate. Plasmas $NF_3/O_2/N_2$ and $NF_3/O_2/Ar$ (solid and hollow symbols, respectively); O_2 and N_2 flows are both 50 sccm, ECR power 750 W.

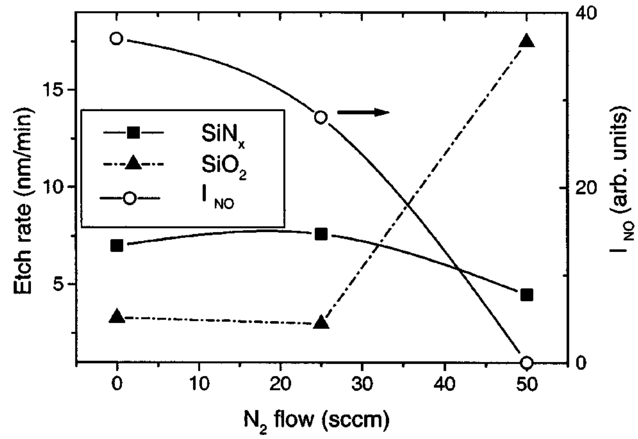

FIG. 3. Etch rate and NO emission intensity vs N_2 flow rate. Plasmas $NF_3/O_2/N_2$; O_2 and N_2 total flow is 50 sccm, ECR power 750 W.

reaches the electrode in an ionized form; this explains the oxide etching reduction. Experiments here were performed at a pressure of 50 mTorr.

Figure 2 shows the etch-rate behavior as small amounts of NF_3 are added to mixtures containing O_2/N_2 or O_2/Ar (both with flows of 50/50 sccm). As can be seen, the SiN_x etch rates rise almost linearly with NF_3 addition, while practically no difference in the etch rate is observed when N_2 is replaced by Ar. In striking contrast to this, up to threefold rise in the SiN_x etch rate was obtained when small amounts of N_2 were added to similar SF_6/O_2 mixtures,[6] evidently due to NO formation in the plasma. This result clearly indicates that for NF_3-based ECR plasmas, the role of NO molecules formed in reactions between oxygen and nitrogen is of less importance. Further results show that the contribution of radicals other than NO (such as NF or NF_2, as well as their ions) is likely to be more important in nitrogen removal and acceleration of the silicon nitride etching. Calculations made using the bond energies data taken from Ref. 12 show that energy released in the surface reaction

$$N_{(surface)}+NF_{(gas)}\rightarrow F_{(surface)}+N_{2(gas)} \tag{7}$$

is slightly higher than that in the reaction (1) with NO (7.4 and 7.0 eV, respectively). Moreover, atomic fluorine produced in reaction (7) is readily absorbed in the surface layer, contributing to further acceleration of the etching process. This is in contrast to the reaction (1), where O atoms, produced as by-products, can be incorporated in the surface reaction layer,[5] hampering etching of silicon atoms. Note that a reaction similar to reaction (7) involving NF_2 radicals is also possible. Probably, the latter mechanism is even more important under the present conditions, in which very weak NF optical emission was observed indicating low NF population in the plasma. NF molecules are known to recombine rapidly generating basically N_2 and F:[13]

$$NF+NF\rightarrow N_2+2F. \tag{8}$$

At the same time, NF_2 radicals recombination may result in formation of N_2F_4:[13]

$$NF_2+NF_2\rightarrow N_2F_4. \tag{9}$$

However N_2F_4 molecules are not stable due to a weak F_2N–NF_2 bond with the dissociation energy of only 0.9 eV,[13] so that a considerable fraction of NF_2 radicals may exist in the ECR plasma.

Figure 3 shows the etch rate as a function of nitrogen content in $NF_3/O_2/N_2$ mixture with 3 sccm flow of NF_3 and the total O_2/N_2 flow of 50 sccm. The dependence of NO γ-emission intensity at 259 nm on N_2 flow is also shown in Fig. 3 (note that for the NF_3/N_2 plasma NO molecules cannot be formed). Emissions from plasma depend on both the densities of plasma species, mechanisms of their excitation and parameters of electrons. At present, we do not have data on the electron density and temperature in the plasma; these measurements will be the subject of future work. However, one can expect that, in the presence of a strongly electronegative gas NF_3, the electron parameters do not change significantly, while O_2 is substituted by N_2. Thus, the NO radical density and its emission intensity are likely to depend similarly on the N_2 flow. An important point is that the SiN_x etch rate variation is relatively small as the gas mixture changes between the NF_3/O_2 and NF_3/N_2 cases (~35% difference) compared with strong variation of the NO emission intensity, suggesting again that the possible NO effect is weak. On the other hand, the Si etch rate depends strongly on the oxygen content in the plasma, being suppressed for oxygen rich mixtures.

In Fig. 4, the effect of small additions of SF_6 to a NF_3/O_2 mixture on the etch rate is presented. It is instructive to compare it with Fig. 5, where NF_3 is added to a SF_6/N_2 mixture. This comparison shows that under the present conditions, NF_3 is much more efficient etcher of SiN_x than SF_6. At the same time, the Si etching depends stronger on SF_6 content in the plasma. This is consistent with our argon actinometry measurements (see the beginning of this section) which have shown that SF_6 is more efficient as a supplier of F radicals as compared with NF_3. More specifically, production of atomic

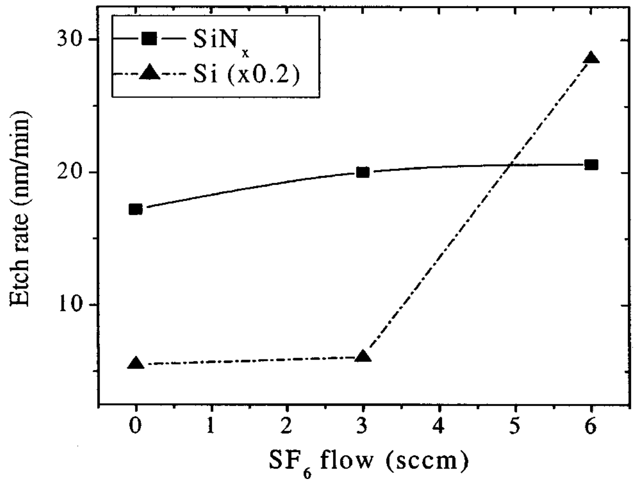

FIG. 4. Etch-rate dependencies on SF_6 flow rate. Plasmas $NF_3/O_2/SF_6$; NF_3 and O_2 flows are 9 and 50 sccm, respectively, ECR power 750 W.

fluorine is 30%–50% less in N_2/O_2-based plasmas containing the same amount of NF_3 compared with SF_6. The facts that the nitride etch rate tends to saturate when SF_6 is added (Fig. 4) and grows quickly with NF_3 content in a situation in which NO molecules cannot be formed (Fig. 5) suggest that the SiN_x etching is limited by the flux of NF_x radicals (the NF_3 dissociation products). A comparison of Figs. 4 and 5 also shows that the Si etching is limited by the F flux (the main SF_6 dissociation product), as can be expected.

The etch-rate dependencies on rf power applied to the lower electrode are presented in Fig. 6. Increasing ion bombardment results in higher etch rates and smaller etching selectivities for both SF_6- and NF_3-based mixtures. When nitrogen is substituted by argon in $SF_6/O_2/N_2$ mixtures, the SiN_x-to-Si etching selectivity reduces considerably, especially for higher rf powers [Fig. 6(a)]. An important point is that while for the SF_6-based mixtures the nitride etching shows a tendency for saturation with high rf powers, its growth is faster than linear for the NF_3-based mixtures [compare Figs. 6(a) and 6(b)]. This indicates that the contribution of ionized NF_x^+ species to etching may be significant in the latter case.

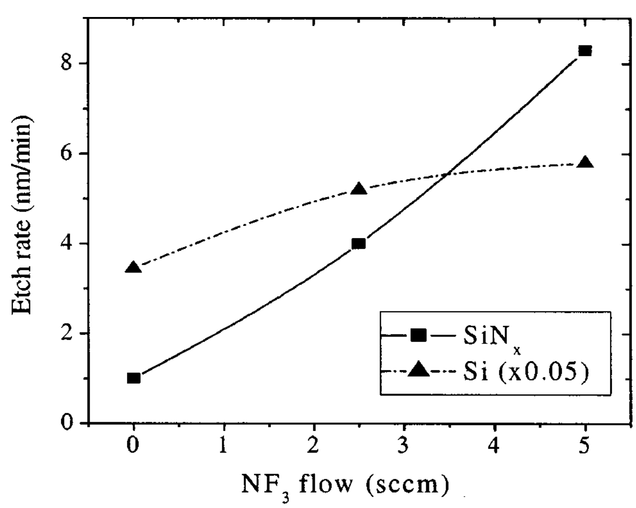

FIG. 5. Etch-rate dependencies on NF_3 flow rate. Plasmas $SF_6/N_2/NF_3$; SF_6 and N_2 flows are 7.6 and 50 sccm, respectively, ECR power 750 W.

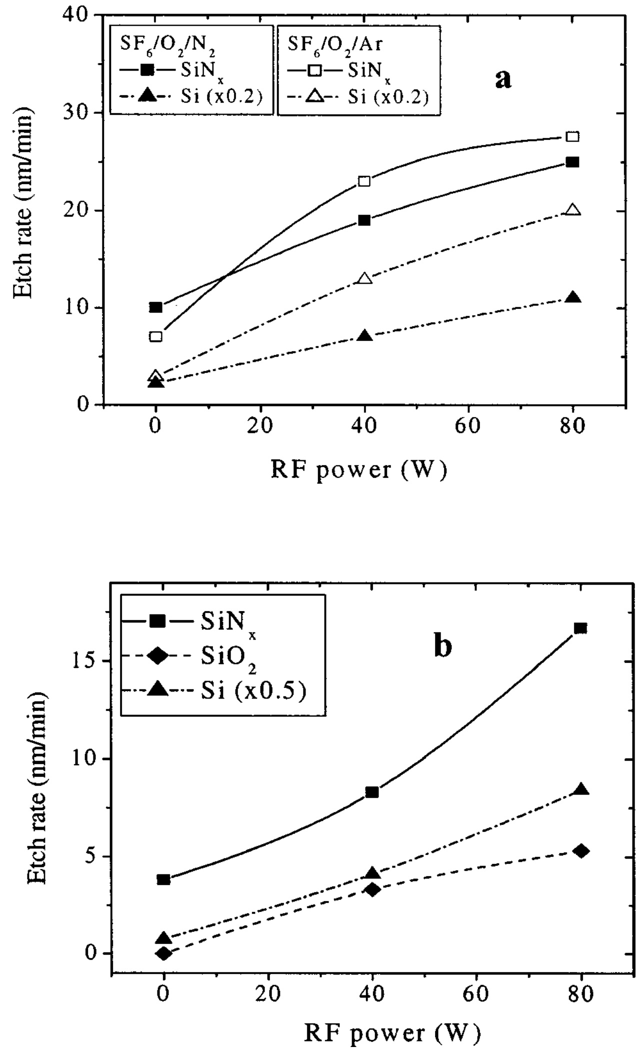

FIG. 6. Etch-rate dependencies on rf power. (a) Plasmas $SF_6/O_2/N_2$ and $SF_6/O_2/Ar$ (solid and hollow symbols, respectively); SF_6 and N_2 flows are 7.6 and 50 sccm, respectively, ECR power 750 W. (b) Plasmas $NF_3/O_2/N_2$; NF_3, O_2 and N_2 flows are 5, 50, and 50 sccm, respectively, ECR power 750 W.

Significant difference in the etch-rate behavior for SF_6- and NF_3-based mixtures is also observed when the ECR power is varied. For the former [Fig. 7(a)], the nitride etch rate rises quickly with ECR power, while only a slight increase occurs for the latter [Fig. 7(b)]. This gives further support to the assumption that main etching precursors are different for the two cases. With increasing ECR power and the feed gases dissociation, NO molecules (generated basically in reactions between N_2 and O) are produced on a larger scale. If NO molecules were the main SiN_x etching precursors, this would contribute to acceleration of nitride etching with ECR power, as production of F radicals also rises with power. In fact, that is the case for SF_6-based plasmas, but it does not happen for NF_3. This means that deeper dissociation of NF_3, occurring at higher ECR power, does

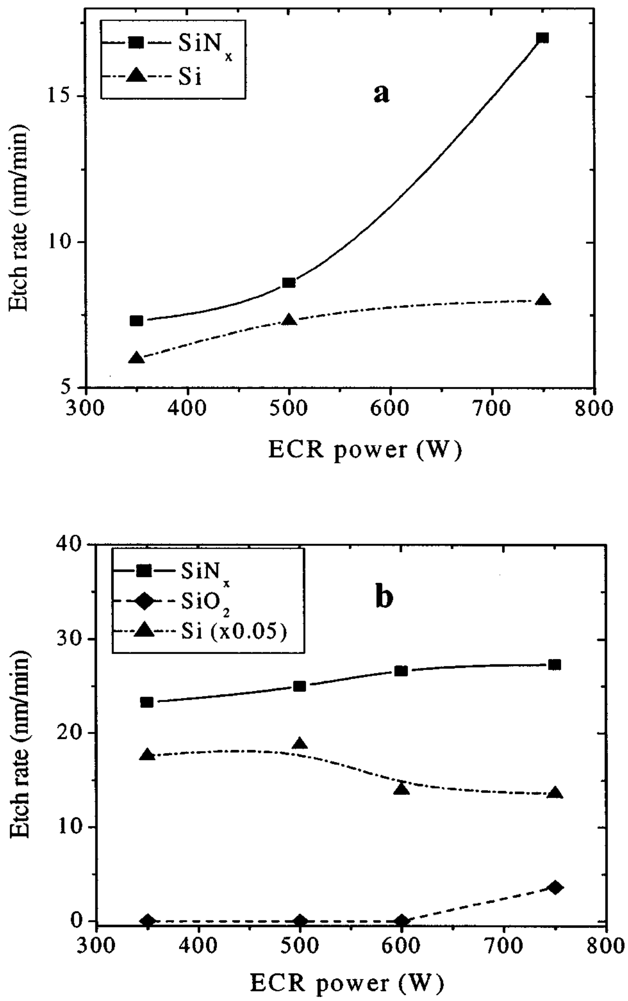

FIG. 7. Etch-rate dependencies on ECR power. (a) Plasmas $SF_6/O_2/N_2$; SF_6, O_2, and N_2 flows are 5, 50, and 10 sccm, respectively. (b) Plasmas NF_3/O_2; NF_3 and O_2 flows are 9.4 and 5 sccm, respectively.

not result in faster SiN_x etching. A possible explanation is as follows. With increasing fraction of the final NF_3 dissociation products (N and F radicals), the net nitride etching reaction probability may decrease, since the process is likely to be less efficient when these atomic radicals react on the nitride surface separately rather than in the form of NF_x radicals (i.e., simultaneously). In other words, a moderate rather then high NF_3 dissociation (when the gas serves as a supplier of both F and NF_x radicals) can be favorable for better gas utilization and faster nitride etching. This is probably the reason for the abnormally fast nitride etching observed in Ref. 14 using NF_3 in high-density plasma etching experiments for untuned or unstable discharges (i.e., at reduced levels of power absorbed in the plasma). Similar effects (enhanced nitride etch rates) were observed in our experiments during unstable operation of the ECR source. It is well known also that low-density plasma discharges are very efficient in cleaning of residues containing silicon nitrides and oxynitrides. In the case of full utilization of NF_3 dissociation products, the net etching reaction would be

$$Si_3N_4 + 4NF_3 \rightarrow 3SiF_4 + 4N_2. \tag{10}$$

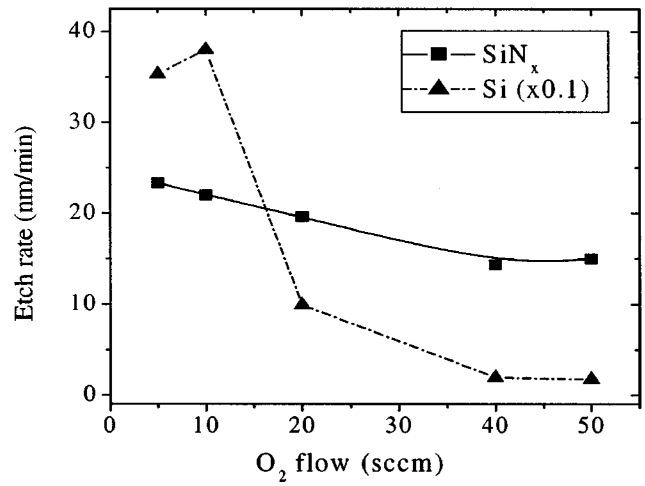

FIG. 8. Etch-rate dependencies on O_2 flow rate. Plasmas NF_3/O_2; NF_3 flow is 9.4 sccm, ECR power 350 W.

An important point is that, whereas NO radicals can be regenerated downstream basically in reaction (3) with long-lived metastable N_2 molecules, NF_x radicals are lost rapidly. Therefore, in remote plasma experiments, the effect of NO on the nitride etching is more evident,[3–5] while the contribution of NF_x radicals is likely to be negligible. On the other hand, in downstream experiments in which the plasma generation zone is close to the reactor zone, as in our case, the NF_x effect is possible.

The fact that the silicon etch rate tends to saturate [Fig. 7(a)] or does not change notably with ECR power [Fig. 7(b)], may be attributed to increasing dissociation of oxygen, which promotes the Si surface oxidation. Note that silicon etching may be additionally suppressed in the presence of NO radicals,[5] while NF_x radicals can only accelerate it. This may explain that lower selectivities over Si were achieved when NF_3 was used as a fluorine source.

The results of experiments performed at low ECR power (350 W) when the NF_3 gas is gradually diluted by oxygen are shown in Fig. 8. It can be seen that the Si etch rate, which is high at a low ECR power level and small O_2 contents, can be reduced considerably for oxygen-rich plasmas, with only slight decrease of the SiN_x etch rate, keeping the oxide etch rate negligible.

IV. CONCLUSIONS

The results of a comparative study of SiN_x, SiO_2, and Si etching in SF_6- and NF_3-based gas mixtures using a high-density ECR plasma are presented. Spectroscopic analysis has shown that spectra emitted from the plasmas containing NF_3, O_2, and N_2 are very similar to those observed for the $SF_6/O_2/N_2$ mixtures. That indicates that the main mechanisms of NO radicals formation in the plasma are the same for both cases. However, etching characteristics appear to be distinctly different for SF_6- and NF_3-based mixtures suggesting different etching mechanisms. In the SF_6 case, best results are achieved in O_2/N_2-rich plasmas in which the nitride etching by fluorine can be enhanced by NO molecules produced in various gas-phase reactions. Analysis of the results obtained shows that the nitride etching in NF_3-based mixtures is more likely to be dominated by NF_x ($x=1$ or 2) radicals in neutral or ionized forms rather than by NO radicals. Possible mechanisms of surface reactions were discussed.

The basic difference between reaction pathways including NO and NF_x radicals is that the former can be regenerated in the downstream region in reactions with long-lived metastable nitrogen molecules, while the latter is lost rapidly and its regeneration is unlikely to occur. That determines a sharp distinction existing between etching regimes using NF_3-based mixtures and obtained with remote plasmas where the NO effect is predominant and in a downstream processing close to the plasma generation zone where NF_x contribution to nitride etching may be significant.

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